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Some underwater acoustical applications require a window that is both acoustically transparent and structurally rigid. No previous material possesses those properties, the closest being "PMP" plastic, whose specific acoustic impedance is 17% higher than seawater. A series of partially fluorinated epoxies is described that have sound speeds near water, but densities that are more than 50% higher than water. When these fluoroepoxies are compounded with glass microspheres to lower their densities, their sound speeds increase too much to permit a match to water. When they are compounded with a mixture of glass microspheres and phenolic plastic microspheres, they achieve both a sound speed and a density match to a water medium. A panel of such a composite had an insertion loss of less than 1 dB from 10 to 100 kHz at normal incidence. The composites have attractive engineering properties. The components are commercially available.

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Some underwater acoustical applications require a window that is both acoustically transparent and structurally rigid. No previous material possesses those properties, the closest being "PMP" plastic, whose specific acoustic impedance is 17% higher than seawater. A series of partially fluorinated epoxies is described that have sound speeds near water, but densities that are more than 50% higher than water. When these fluoroepoxies are compounded with glass microspheres to lower their densities, their sound speeds increase too much to permit a match to water. When they are compounded with a mixture of glass microspheres and phenolic plastic microspheres, they achieve both a sound speed and a density match to a water medium. A panel of such a composite had an insertion loss of less than 1 dB from 10 to 100 kHz at normal incidence. The composites have attractive engineering properties. The components are commercially available.

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INTRODUCTION

There are a number of underwater acoustical applications that require the use of a material that both rigidly supports some component and produces minimal interference with the acoustic wave. One example is the requirement that a nearfield calibration array using piezoelectric polymer as its active element be acoustically transparent so as to avoid setting up standing waves between the array and the transducer being calibrated. The piezoelectric polymer is essentially transparent at desired operating frequencies of the array. Thus the transparency of the material used to support the polymer is even more important. But the mounting material must be structurally rigid since the thin piezoelectric polymer film must be precisely positioned. Another application that requires a rigid and acoustically transparent window material is weapons transducers that operate at relatively high frequencies, but also may be subjected to high stresses induced by hydrodynamic flow. In addition, there are numerous applications where a rigid window in a structure presents engineering advantages.

Structural rigidity carries with it the implication that the material has a relatively high shear modulus. On the other hand, acoustical transparency requires that the material have a sound speed (or more precisely, bulk longitudinal wave speed) and density that matches the water medium in which it is submerged. Having a sound speed and density matching water, in turn, means that the adiabatic bulk modulus (density times sound speed squared) is relatively low. Ordinary polymer materials that have a sound speed and density match with water have correspondingly low shear moduli. Typical is a lightly filled natural rubber, wherein the sound speed is 1524 m/s and the density is 1038 kg/m³—an excellent match to water; this material has a Young's modulus of 1.1 MPa (at 2 kHz and 25 °C) and is, consequently, pliant rather than rigid.

A number of researchers have sought a material that is

structurally rigid, but acoustically transparent. One material that lends itself to this goal is poly(4-methyl-pentene), or PMP. The acoustical properties of PMP were measured at the Naval Surface Warfare Center.¹ PMP has a sound speed of 2180 m/s, but a density of only 835 kg/m³; the specific acoustic impedance is thus only 17% higher than seawater at 1.82×10^6 Rayl. Montgomery *et al.*² showed that when soft epoxies were blended with hard epoxies, the sound speed and density are indeed reduced, but it is only after the epoxies are no longer rigid that they approach acoustical transparency in seawater.

Thompson and Ting³ showed the relatively minor effect on sound speed of a change in epoxy curative or of the use of a partially brominated epoxy. A more pronounced, but still inadequate, lowering of sound speed was seen when the epoxy was toughened by the addition of rubbery inclusions in the formulation.

The latter paper, as well as others,^{4,5} reported that a series of partially fluorinated epoxy compounds has sound speeds that are good matches with seawater. However, these compounds all have densities that are significantly greater than 1000 kg/m³. The work reported here is that which went into developing these fluoroepoxies so that they were practical materials that matched both the sound speed and density of the seawater medium.

I. EXPERIMENTAL

A. Materials

The chemical formula of the fluoroepoxy resin discussed here is shown in Fig. 1.

The C_r group in this structure refers to a perfluorinated normal alkyl group with a chain length of from 0 to 11 carbons. Samples were made from fluoroepoxy resins containing several different lengths of side chains: with no side chain (C-0), with a 6-carbon side chain (C-6), with an 8-carbon

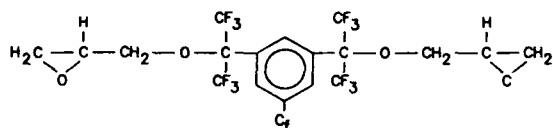


FIG. 1. Structural formula of the fluoroepoxy resin.

side chain (C-8), or with a mixture of 9- and 11-carbon side chains (C-9;C-11).

Common epoxy-curing agents are not soluble in the fluoroepoxy resin and thus cannot produce a usable cured product. The material, bis(3-aminopropyl)tetramethyldisiloxane (referred to as silicone amine) has been found to become compatible with the fluoroepoxies after brief heating with the resin and has produced samples with good strength.⁶ Analogs of this siloxane with longer Si-O-Si chains may also be used to produce a material with lower rigidity. A second curative that has been developed for curing the fluoroepoxy resins is a partially fluorinated anhydride⁷ with the formula, 4-hexafluoroisopropylideneol phthalic anhydride. Also shown to be a useful curing agent is an adduct prepared by the reaction of excess ethylene diamine with the fluoroepoxy resin containing a 6-carbon side chain (i.e., C-6). All curatives were used in stoichiometric amounts. This means that each ionizable hydrogen in the structure of the curing agent is assumed to be active.

The fluoroepoxy resins used in this work were synthesized by a number of chemical companies working under license to the Naval Research Laboratory. The C-8 fluoroepoxy resin is commercially available from Allied-Signal, Inc., P. O. Box 2332R, Morristown, NJ 07960. The silicone amine discussed is available as No. B1710 from Petrarch Systems, Inc., Bartram Road, Bristol, PA 19007.

An example of preparation of a sample using the silicone amine curative follows: 23.5 g of the C-8 fluoroepoxy resin was degassed, and 3.10 g of the silicone amine was added. The mixture was warmed to 55° in a water bath and stirred vigorously until a single phase was produced (typically 7-8 min). Any microspheres were then stirred in and the mixture was again degassed under vacuum for a few minutes. The mixture was poured or troweled into the mold and cured at 40° for 1-2 h. The materials were post-cured at 75° overnight. Some care is necessary to keep the microspheres from floating upward before the mixture cures to a viscosity high enough to prevent this. This segregation may be avoided by periodically or constantly rotating the mold. Small, uniform samples have also been made by stirring just before the mixture gels. The adduct curative discussed is prepared by the reaction of an excess of ethylene diamine with the C-6 fluoroepoxy resin and removing the unreacted ethylene diamine. An example of sample preparation with this curative is: Degass 23.5 g of the C-8 resin, and add 8.00 g of the adduct curative. Stir in the weighed quantity of microspheres and degas. Place the mixture into the mold and cure for 1-2 h at 40°, again being careful to avoid flotation of the microspheres. Postcure at 75° overnight. The high-strength glass microspheres are "IGD-101" made by Emerson and Cuming, Inc. The phenolic microspheres are "BJO-0840" made

by Union Carbide Corporation's Specialty Chemicals Division.

B. Methods

The sound-speed measurements reported were performed on a singaround velocimeter operating at a frequency of 1.5 MHz and at a temperature of 25 °C. This method is similar to that of Zacharias *et al.*⁸ The typical standard deviation on a single sample is 0.5 m/s. The sound speeds reported at these high measurement frequencies are probably very close to those that would be obtained at lower frequencies. The fluoroepoxies are well below their glass transition temperature even at low frequency. Thus the higher measurement frequency is on the same plateau of the modulus versus temperature curve. Densities were measured by an Archimedeian method.

II. RESULTS AND DISCUSSION

A. Acoustical properties of neat fluoroepoxy resins

The fluorinated materials mentioned above were developed at the Chemistry Division of the Naval Research Laboratory (NRL).^{9,10} These fluoroepoxies have many of the characteristic properties of fluorine-containing organic compounds such as a low surface energy, but they also have most of the important properties of ordinary epoxy resins such as ease of handling and good engineering properties.¹¹ Samples were prepared of fluoroepoxy resins of several different side chain lengths and with the three different curatives. Table I gives the measured sound speeds and densities of these samples.

Comparison of the data for samples cured with the fluoroanhydride with those of the same resin cured with silicone amine or with the adduct curative shows that the fluoroanhydride curative causes a significant increase in sound speed. The silicone amine and the adduct curative produce samples with about the same sound speeds, but the adduct does increase the density somewhat. An 8-carbon side chain length yields a material with a near-optimum sound speed.

B. Acoustical properties of fluoroepoxy composites

Attempts to produce composites of these epoxies with ordinary glass microspheres were unsuccessful. When a

TABLE I. Sound speeds at 1.5 MHz and densities for neat fluoroepoxy resins cured with silicone amine (Si), or with ethylene diamine adduct, or with fluoroanhydride. The "C-X" designation means an NRL fluoroepoxy with a side chain X carbons long.

Fluoroepoxy		Density, 25 °C (kg/m ³)	Sound speed, 25 °C (m/s)
C-0,	fluoroanhydride cure	1608	2039
C-6,	silicone amine cure	1562	1577
C-6,	fluoroanhydride cure	1668	1735
C-8,	silicone amine cure	1591	1513
C-8,	fluoroanhydride cure	1682	1675
C-8,	adduct cure	1684	1516
C-9,C-11,	silicone amine cure	1578	1529

C-9;C-11 resin with silicone amine curative was prepared with glass microspheres, the density was determined to be 1290 kg/m^3 instead of 1000 kg/m^3 , as expected from the densities of the starting materials. The high density of the composite apparently results from the fracturing of most of the microspheres during the vacuum degassing step. Only high-strength glass microspheres, which do not disintegrate under vacuum, were used in the further work.

A sample of C-8 fluoroepoxy resin cured with silicone amine was compounded with 13.6% by weight of high-strength glass microspheres. The density for this sample was calculated to be 1000 kg/m^3 from the density of the resin and an assumed density for the microspheres. The measured density was 977 kg/m^3 . The sound speed of this sample was 1759 m/s . A series of samples was prepared from adduct-cured C-8 fluoroepoxy resin containing a range of concentrations of high-strength glass microspheres. The sound speeds and densities of these are shown in Fig. 2.

The glass microspheres clearly cause a regular and significant increase in the sound speed of the composite. This is in contrast to data tabulated for composites of ordinary DGEBA epoxies,¹² where the presence of glass microspheres caused a decrease in sound speed.

The high sound speed of the samples that have sufficient glass microspheres to reduce the density to 1000 kg/m^3 clearly implies that a softer microsphere will be necessary to keep the sound speed from increasing with increasing microsphere content. One such softer microsphere is made from phenolic resin. A series of fluoroepoxy samples was prepared from the C-8 resin cured with the adduct curative and containing a range of concentrations of phenolic microspheres. Their sound speeds and densities were measured and are depicted in Fig. 3.

These soft microspheres clearly cause a substantial reduction in the sound speed of the composite. Consequently, a combination of the two types of microspheres suggests itself as a filler. Since the presence of approximately 12% by weight of glass microspheres increases the sound speed of the resin by 230 m/s and the presence of about 12% of phenolic

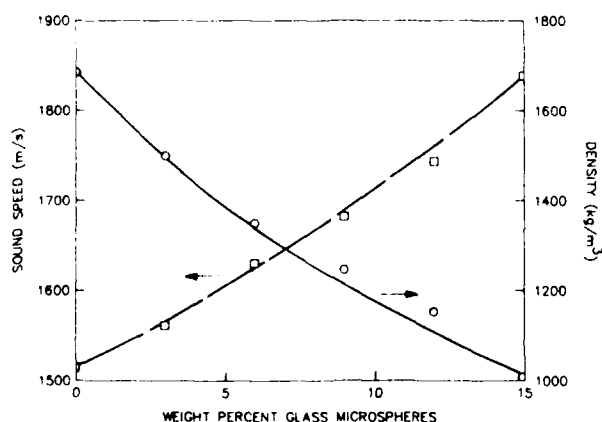


FIG. 2. The sound speeds and densities of adduct-cured fluoroepoxies filled with high-strength glass microspheres. The lines given for each property are those generated for a larger data set explained below.

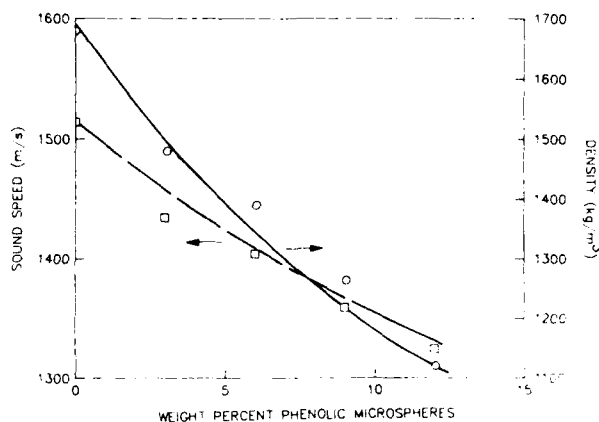


FIG. 3. The sound speeds and densities of adduct-cured fluoroepoxies filled with phenolic resin microspheres.

microspheres decreases the sound speed by 190 m/s , it appears that approximately equal amounts of the two fillers would be a reasonable first guess to achieve a composite with a sound speed near 1500 m/s . Indeed, a sample containing 6.45% by weight of each of these two types of microspheres was found to have a sound speed of 1523 m/s and a density of 1062 kg/m^3 . A number of samples were prepared from C-8 fluoroepoxy resin cured with the adduct, near a one-to-one ratio of the two microspheres and in the 14%–16% range of total concentration of microspheres. The data sets for sound speed and density of these samples are difficult to represent since they consist of two independent variables controlling one dependent variable. The approach taken here was to develop empirical equations to describe the variation in acoustical property with composition.

The density data on this series of samples and the density data on the resin containing only one type of microsphere were fitted to an equation of the form

$$\text{composite density} = 100 / \left[(\text{wt. \% glass} / \text{density glass}) + (\text{wt. \% phenolic} / \text{density phenolic}) + (\text{wt. \% resin} / \text{density resin}) \right]. \quad (1)$$

There is no convenient statistical least-squares fitting program available for such a three-dimensional data set. Consequently, a fit of this equation to the density data set was done by iteratively adjusting the three densities until the error squared was minimized. The starting values for the iteration were the microsphere manufacturer's approximate densities and the density measured for the neat resin. The iterative procedure converges to the following values for the densities of the individual components:

density phenolic microspheres: 315.7 kg/m^3 ;

density glass microspheres: 314.1 ;

density resin: 1700 .

The coefficient of correlation with these values is 0.983 . These density values for the microspheres are both in the range given by their manufacturers. The resin density is near, but slightly higher than, the density measured for the neat resin. The lines that were given in Figs. 2 and 3 for

densities of samples containing only one type of microsphere are plots of Eq. (1) with the least-squares-fitted coefficients.

The coefficients of a least-squares fit for a quadratic equation through the sound speeds of fluoroepoxy samples containing only glass microspheres and the similar coefficients for samples containing only phenolic microspheres were used as starting coefficients for an iterative least-squares fit of the three-dimensional data to a quadratic equation of the form

$$\begin{aligned} \text{sound speed} = & a + b (\text{wt.}\% \text{ glass balloons}) \\ & + c (\text{wt.}\% \text{ phenolic balloons}) \\ & + d [(\text{wt.}\% \text{ glass})^2 \\ & + (\text{wt.}\% \text{ phenolic})^2] \end{aligned} \quad (2)$$

The average of several sound-speed determinations on neat fluoroepoxy samples was assigned as the a term. The error squared of the entire data set of 26 samples converged to a minimum value after approximately 300 iterations. At this point, the coefficient of correlation was 0.980. The coefficients at the minimum are $a = 1516$ (assigned), $b = 16.09$, $c = -19.82$, and $d = 0.377$. The lines for sound speeds shown in Figs. 2 and 3 for samples containing only one type of microsphere are those of Eq. (2) with the least-squares-fitted coefficients.

It was clear in making and measuring the samples that those with total microsphere contents above about 15% contained some entrained air. In some cases, air voids could be found when the samples were sanded flat. In other cases, the sound-speed-measuring pulse was attenuated too much to permit measurement. Consequently, a significant error in the sound speeds of these samples might be anticipated. Fig-

ure 4 depicts the absolute value of the difference between the measured and the calculated sound speed versus the total microsphere content. There is shown to be a general trend to larger sound-speed errors at high microsphere contents.

A microsphere content of 15% corresponds to a density of near 1000 kg/m^3 for an adduct-cured fluoroepoxy. The large error that is sometimes seen in samples with this many microspheres must be taken as a warning that extra care must be taken in preparing parts near this composition. The most notable way in which the fluoroepoxy composites differ from other composites is the fluoroepoxy composites' very large shrinkage on curing. If a method of maintaining a substantial positive pressure is provided, the problem of air voids can be eliminated. The fluoroepoxy resin has a high air solubility, and a positive pressure will cause any entrapped air to dissolve into the matrix during the cure process. Such a method was used to prepare the subsequent samples.

The two equations with their coefficients will provide guidance in designing a composite material with a chosen sound speed and density. For example, assume that a sound speed of 1490 m/s and a density of 1000 kg/m^3 are desired to match a fresh water medium; simultaneous solution of Eqs. (1) and (2) shows that a fluoroepoxy composite containing 9.22% phenolic microspheres and 6.70% glass microspheres will have these properties. For a match with seawater at a sound speed of 1530 m/s and a density of 1030 kg/m^3 , a composite containing 7.38% phenolic microspheres and 7.40% glass microspheres will be required.

C. Panel test

A panel was prepared from filled, silicone amine-cured C-8 fluoroepoxy. The fillers were 5.5% glass microspheres

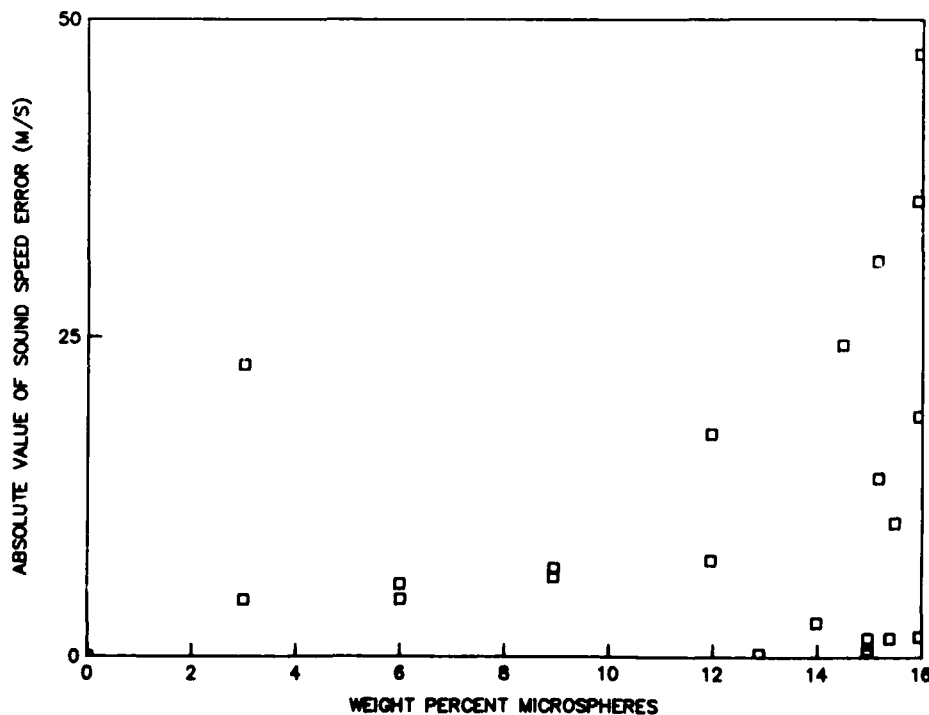


FIG. 4. Absolute value of the difference between the measured sound speed for fluoroepoxy samples and the sound speed calculated by Eq. (1).

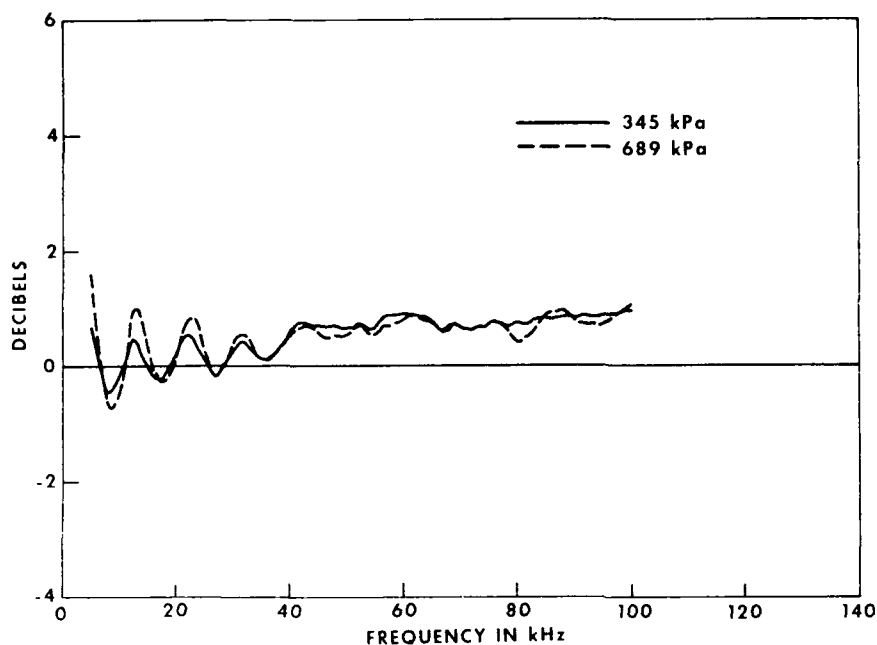


FIG. 5. Insertion loss at normal incidence of a $40 \times 40 \times 1.9$ -cm panel of C-8 fluoroepoxy resin filled with 5.5% glass microspheres and 6.4% phenolic microspheres and cured with a silicone amine. The solid line represents the insertion loss measured at 345 kPa and the dashed line at 689 kPa.

and 6.4% phenolic microspheres. The lower total microsphere content is a result of the lower density of the silicone amine-cured fluoroepoxy compared with the adduct curative. The panel dimensions are $40 \times 40 \times 1.9$ cm. Laboratory-sized samples of this composition were determined to have a sound speed of 1490 m/s and a density of 1033 kg/m^3 .

The insertion loss of this panel was measured by the procedure discussed by Bobber.¹³ The measurements were made as a function of frequency at several angles of incidence. Its insertion loss at normal incidence is shown in Fig. 5.

The data reported below about 10 kHz are undoubtedly contaminated by edge diffraction. The insertion loss of this

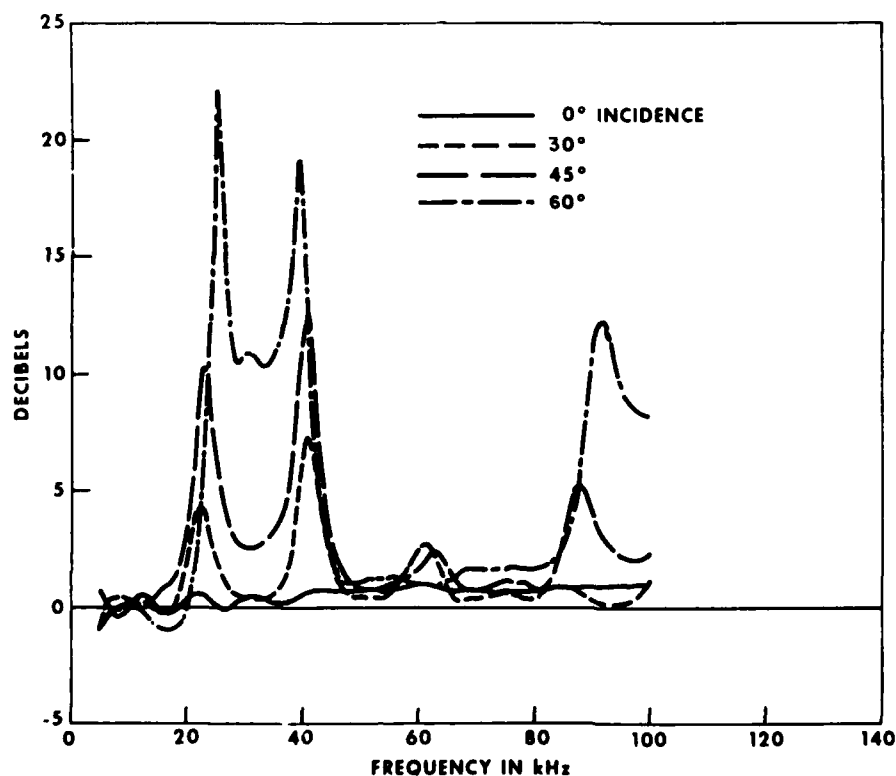


FIG. 6. Insertion loss at oblique incidence angles of a $40 \times 40 \times 1.9$ -cm panel of C-8 fluoroepoxy resin filled with 5.5% glass microspheres and 6.4% phenolic microspheres and cured with a silicone amine. The measurements were taken at 22°C and 345 kPa: —, 0° or normal incidence; ---, 30° incidence; - · -, 45° incidence; and - - -, 60° incidence.

panel at oblique incidence angles is shown in Fig. 6.

The insertion loss shown below about 10–20 kHz (depending on the incidence angle) is likewise contaminated by edge diffraction. At oblique incidence angles, of course, there is considerably more conversion to shear modes in the panel. The data on this panel were previously reported by Dubbelday and Rittenmyer¹⁴ who used them as an illustration of their method of calculation of the interferences caused by shear resonances. They interpreted the peaks in the insertion loss of this panel as arising from the panel's thickness shear resonance. This mode's contribution is a consequence of the high shear modulus of this material. The magnitude and frequency of these peaks are dependent on the panel thickness, and on the precision of the sound speed and density match to the medium, and to a minor extent on the lateral dimensions of the panel. Thus it might be surmised that, in the design of a window for a specific frequency range, the thickness or composition of the fluoroepoxy composite may be adjusted to provide for very low insertion loss, even at off-normal angles of incidence.

III. CONCLUSIONS

Materials have been developed that are structurally rigid and yet have plane-wave sound speeds and densities that match either a fresh water or a seawater medium. The insertion loss at normal incidence of one of the composite materials is shown to be less than 1 dB over a 10- to 100-kHz frequency range. At oblique incidence, shear-wave phenomena cause peaks in the insertion loss of this material at specific frequencies. The components of these composites are now commercially available.

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